

Week 4

IDEAL AND REAL SOLUTIONS 1

Thermodynamics of Mixing

Partial pressures are useful in the study of mixing of gases. To study mixing in solution, we need analogous partial properties.

Partial Molar Volume

The contribution a particular component makes to the total volume of the sample.

Partial volumes of the components vary with composition, hence the thermodynamics varies with composition.

The partial volume is defined by an equation analogous to the chemical potential of a component and of the partial pressure of a component.

$$V_J = \left(\frac{\partial V}{\partial n_J} \right)_{p, T, n'}$$

The partial volume of component J , V_J , is the rate of change in the total volume with change in component J at constant p , T , and every other component n' (or the slope or a plot of the total volume vs the amount of J).

The total volume is the sum of the partial molar volumes of all the components each multiplied by the number of moles of each component.

$$V = n_A V_A + n_B V_B + \dots$$

Partial Molar Gibbs Energy

The concept of partial molar quantities can also be extended to cover any state functions. We have already met the molar Gibbs Energy – it is the chemical potential.

$$\mu_J = \left(\frac{\partial G}{\partial n_J} \right)_{p, T, n'}$$

The slope of total Gibbs energy vs amount of J .

The total Gibbs energy is the sum of the chemical potentials (molar Gibbs energies) of all the components each multiplied by the number of moles of each component.

$$G = n_A \mu_A + n_B \mu_B + \dots$$

As G is p and T dependent, for a mixture of A, B, ..., etc., $dG = Vdp - SdT$ becomes:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

At constant p and T , this simplifies to:

$$dG = \mu_A dn_A + \mu_B dn_B + \dots,$$

Which, since under these conditions $dG = dw$, implies,

$$dw = \mu_A dn_A + \mu_B dn_B + \dots$$

That is, additional non p-V work can arise from changing the composition of the system.

Significance of the Chemical Potential

With the chemical potential we can generalise the expression for the internal energy change, $dU = TdS - pdV$, to systems in which the composition may change

$$dU = TdS - pdV + \mu_A dn_A + \mu_B dn_B + \dots$$

This implies that at constant volume and entropy,

$$\mu_J = \left(\frac{\partial U}{\partial n_J} \right)_{V, S, n'}$$

Which by analogy means for enthalpy and Helmholtz energy:

$$\mu_J = \left(\frac{\partial H}{\partial n_J} \right)_{p, S, n'} \qquad \mu_J = \left(\frac{\partial A}{\partial n_J} \right)_{V, T, n'}$$

The chemical potential shows how U , H , A , and G change under the appropriate conditions.

Gibbs-Duhem Equation

Because G is a state function,

$$\sum_J n_J d\mu_J = 0$$

This implies the chemical potential of one component of a mixture cannot be varied independently of the chemical potentials of the other components (*i.e.*, for a binary mixture, as one goes up the other goes down by a corresponding amount).

Thus for a mixture of two components,

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A.$$

This reasoning applies to all partial molar quantities, thus with the analogues of $G_m = \mu$, we can use the analogues of the Gibbs-Duhem equation to determine the value of one partial molar quantity by measuring the another.

Gibbs Energy for Mixing Perfect Gases

The chemical potential μ for a pure gas is:

$$\mu = \mu^0 + RT \ln p,$$

where p is the pressure relative to the standard pressure of one bar (*i.e.*, p = actual pressure over one bar = the pressure in bar rather than Pascals), and the standard chemical potential is that for the gas at the standard pressure (1 bar).

For a mixture of two pure gases A and B, we can obtain the Gibbs energy of the pure A and pure B from the equation for the chemical potential above. Thus, the Gibbs energy of mixing is

$$\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}.$$

Which in terms of mole fractions ($p_J/p = x_J$) is:

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

Because x_J is not greater than 1, $\ln x_J$ is negative. This implies Gibbs energy of mixing is negative ($\Delta_{mix} G < 0$), and thus, mixing is spontaneous. We know this from common sense, but now we can discuss it qualitatively.

This argument can be extended to other thermodynamic quantities, *e.g.*, enthalpy, entropy, internal energy, Helmholtz energy.

$$\Delta_{mix} S = \left(\frac{\partial \Delta_{mix} G}{\partial T} \right)_{p, n_A, n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

Because $\ln x_J < 0$, $\Delta_{mix} S > 0$ for all components.

The above two examples also imply $\Delta_{mix} H = 0$.

Chemical Potentials of Liquids

Ideal solutions

Let $\mu_A^*(l)$ be the chemical potential of pure liquid A, and $\mu_B^*(l)$ be the chemical potential of pure liquid B. *etc.*

Then the vapour pressure of pure A is p_A^* and thus, its chemical potential is

$$\mu_A^* = \mu_A^0 + RT \ln p_A^*$$

Now add a solute to the pure liquid A. Its chemical potential change from its pure value to μ_A . The vapour pressure is now

$$\mu_A = \mu_A^0 + RT \ln p_A$$

Experimentally it is found that the ratio of the partial pressure of each component of a mixture to its vapour pressure as a pure liquid is to a good approximation equal to its mole fraction. This relationship, $p_A = x_A p_A^*$ is known as *Raoult's law*.

Combine the above to eliminate μ_A^0 and using Raoult's law leads to

$$\mu_A = \mu_A^* + RT \ln x_A$$

This equation is the definition of an ideal solution.

Raoult's law is not always obeyed. However, even in such cases, the approximation becomes very good as p_A approaches p_A^* ; *i.e.*, for dilute solutions.